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SYNTHESIS OF LANTHANUM CHROMITE USING THE SOL-GEL METHOD

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Synthesis of lanthanum chromite using the sol-gel method is considered. The effect of the amount of gel-forming agent and the heat treatment time and temperature on the completion of synthesis is investigated. The optimum parameters of the process are presented. The possibility of replacing the powder obtained by vibration crushing of electrically melted lanthanum chromite with powder synthesized by the sol-gel method in the production of miniature ceramic articles is demonstrated.

Lanthanum chromite is of interest as a material for engineering ceramic production (resistive electric heaters, thermal transformers, sensors etc.)

The known methods of lanthanum chromite production are based on solid-phase synthesis reaction at a temperature above 1000°C or liquid-phase synthesis with high-frequency melting at temperature above 2500°C with subsequent grinding [1, 2]. A decrease in the temperature of lanthanum chromite synthesis is achieved by using solutions of oxygen-containing lanthanum and chromium compounds as the initial reagents, with subsequent evaporation and calcination, which makes it possible to mix the reagent at the molecular level. However, due to the different solubility of the reagents in a particular solvent, a mixture of reagent crystals heterogeneous in composition and size is produced on evaporation.

The purpose of the present work is to eliminate the disadvantage mentioned using the sol-gel method. The application of this method makes it possible to synthesize a reaction mixture with preassigned stoichiometry, homogeneous over its entire volume. After calcination, a product in the form of a highly disperse powder with increased grain defects and, consequently, active in sintering, is formed [3]. The gel-like state of the reaction mixture can be used for depositing it as a film on a ceramic or metal substrate and obtaining after firing a coating with prescribed composition.

The gel-forming agent used in the present investigation was a high-molecular-weight compound, namely, polyvinyl alcohol (PVA), introduced in a mixture of aqueous solutions of the initial reagents. The crystals emerging in the course of evaporation are uniformly distributed over the three-dimensional gel lattice. It ensured homogeneity of the composition and sizes of the powdered product after calcination of the gel.

The materials used in synthesis of lanthanum chromite were lanthanum nitrate hexahydrate $La(NO_3)_3 \cdot 6H_2O$ (chemically pure grade); chromium nitrate (III) nonahydrate $Cr(NO_3) \cdot 9H_2O$ (analytically pure grade), PVA $(-CH_2CH(OH)-)_n$ (molecular mass of 200 – 500 g/mole).

The lanthanum and chromium nitrates were separately dissolved in water, then the solutions were mixed in the ratio of $La^{3+} : Cr^{3+} = 1$, and PVA was added in ratios from 0.3 : 1 to 1 : 1 between PVA mass and the rated mass of the resulting product ($LaCrO_3$) with subsequent stirring for 0.5 h and exposure until a gel formed. The gel was dried at a temperature of 100 – 170°C up to formation of xerogel that was later calcined at a temperature of 700 – 900°C, producing $LaCrO_3$ powder.

Release of gaseous products indicated that the interaction between the reagents started at a temperature around 50°C. The scheme of the process at this temperature without taking into account the exact composition of the reaction products can be represented by the following equation:

$$La(NO_3)_{3,\,sol} + Cr(NO_3)_{3,\,sol} + (-CH_2CHOH-)_n = La(OH)_3 + Cr(OH)_3 + C + CO_2 + 6NO_2 + 2nH_2O.$$

According to the results of an approximate thermochemical calculation for the temperature of 25°C, the reaction is endothermic, and its enthalpy is equal to about 150 kJ/mole.

The interaction of the lanthanum and chromium compounds began in the solid phase (xerogel) at a temperature above 300°C, which is supported by the thermal analysis data (Fig. 1). Analysis of the thermograms makes it possible to suggest that the formation of lanthanum chromite pro-

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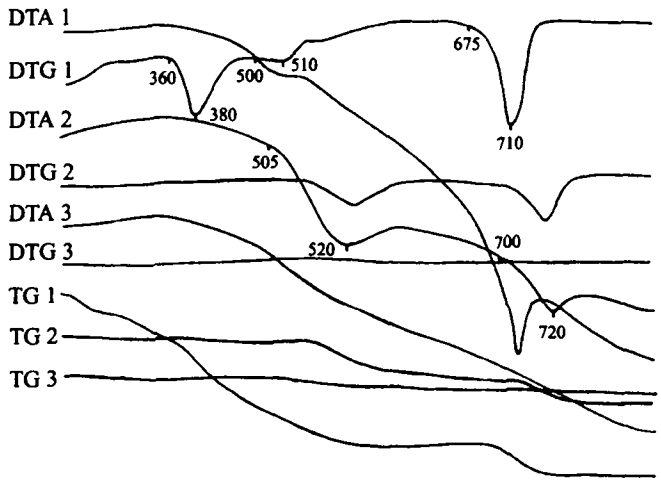

Fig. 1. Derivatogram of samples of reaction mixture xerogel heat treated at temperatures of 300°C (*1*), 500°C (*2*), and 700°C (*3*).

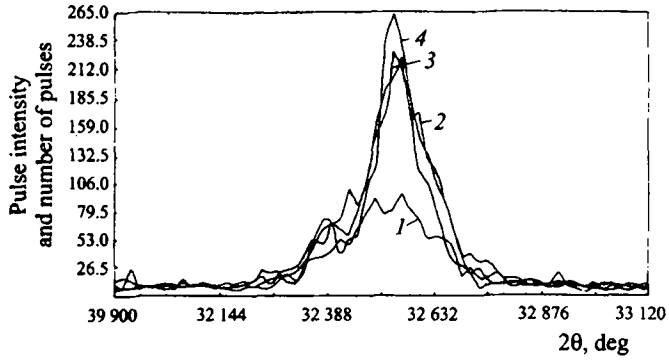

Fig. 2 Analytical fragment of $LaCrO_3$ x-ray patterns ($CuK_{\alpha 1}$ radiation): *1 – 4*) see Table 2.

ceeded via intermediate chromates with a chromium oxidation degree of more than 3+, which is attested by the clearly expressed endothermic effect at temperatures of 675 – 720°C corresponding to their decomposition, producing $LaCrO_3$ [4, 5]. The exothermic effects of chromate formation were not recorded, probably because of their being disguised by the endothermic effects of decomposition of the crystal hydrates of the chromium and lanthanum nitrates. Experiments with xerogel calcination revealed the effect of the treatment time on the completion of synthesis. Thus, at a temperature of 700°C, formation of $LaCrO_3$ ended in 1 h.

The effective content of PVA in the reaction mixture was determined by the x-ray phase analysis and chemical analysis of the product. On introducing PVA in an amount providing for a PVA : $LaCrO_3$ ratio equal to 1 : 1, the end product contained some intermediate compounds that had not reacted. The results of x-ray phase analysis of the product of synthesis are given in Table 1. The best results in completion of synthesis were attained for a PVA : $LaCrO_3$ ratio equal to 0.3 : 1. It is significant that the same concentration of PVA provides for the best crystallization of lanthanum chromite. It is further supported by the fact that with an increase in the PVA content, the absolute intensity of the main analytical peak (d = 0.2745 nm) increases (Fig. 2 and Table 2). The experiments in synthesis established that a temperature below 800°C is insufficient for generation of a highly disperse powder homogeneous in composition and in size.

The size parameters of the powder were investigated with an Analysette-22 analyzer produced by Fritch. The powder size distribution improves with an increase in the PVA : $LaCrO_3$ ratio from 0.3 : 1 to 1 : 1 (Fig. 3). The specific surface area of the powder increased with an increase in the PVA content from 1.68 m^2/cm^3 for PVA : $LaCrO_3$ = 0.3 : 1 to 4.37 m^2/cm^3 at the ratio of 1 : 1 for the same components. It is evidently related to more developed gel formation with an increase in the PVA content. An increase in the xerogel calcination temperature also improves the powder homogeneity (Fig. 3). The specific surface area increases from 1.2 m^2/cm^3 at the temperature of 800°C to 1.68 m^2/cm^3 at 900°C. It is probably due to a more complete destruction (dispersion) of xerogel in calcination. This is the reason for selecting 900°C as the calcination temperature, rather than 700°C which, according to DTA data, seemed sufficient regarding phase formation and yet did not allow for the required dispersion of the synthesized lanthanum chromite powder.

The lanthanum chromite powder obtained by the sol-gel method differed in crystal habitus and grain size from the vibration-crushed $LaCrO_3$ powder synthesized by high-frequency melting. The analysis of the powders on a BS 340 scanning electron microscope (TESLA company) revealed

TABLE 1

Experiment	Synthesis parameters: temperature, °C	Synthesis parameters: PVA : $LaCrO_3$	Product phase composition
1	700	1 : 1	$LaCrO_3$, La_2O_3, indefinite phase
2	800	1 : 1	$LaCrO_3$, Cr_2O_3, indefinite phase
3	900	1 : 1	$LaCrO_3$, Cr_2O_3
4	900	0.6 : 1	$LaCrO_3$
5	900	0.3 : 1	The same

TABLE 2

Curve in Fig. 2	Synthesis parameters: temperature, °C	Synthesis parameters: PVA : $LaCrO_3$	Peak intensity, number of pulses	Peak half-width, deg	Integral area under the curve, number of pulses
1	700	1 : 1	95	0.234	19.7
2	800	1 : 1	225	0.158	41.8
3	800	0.6 : 1	229	0.154	40.2
4	800	0.3 : 1	265	0.100	36.2

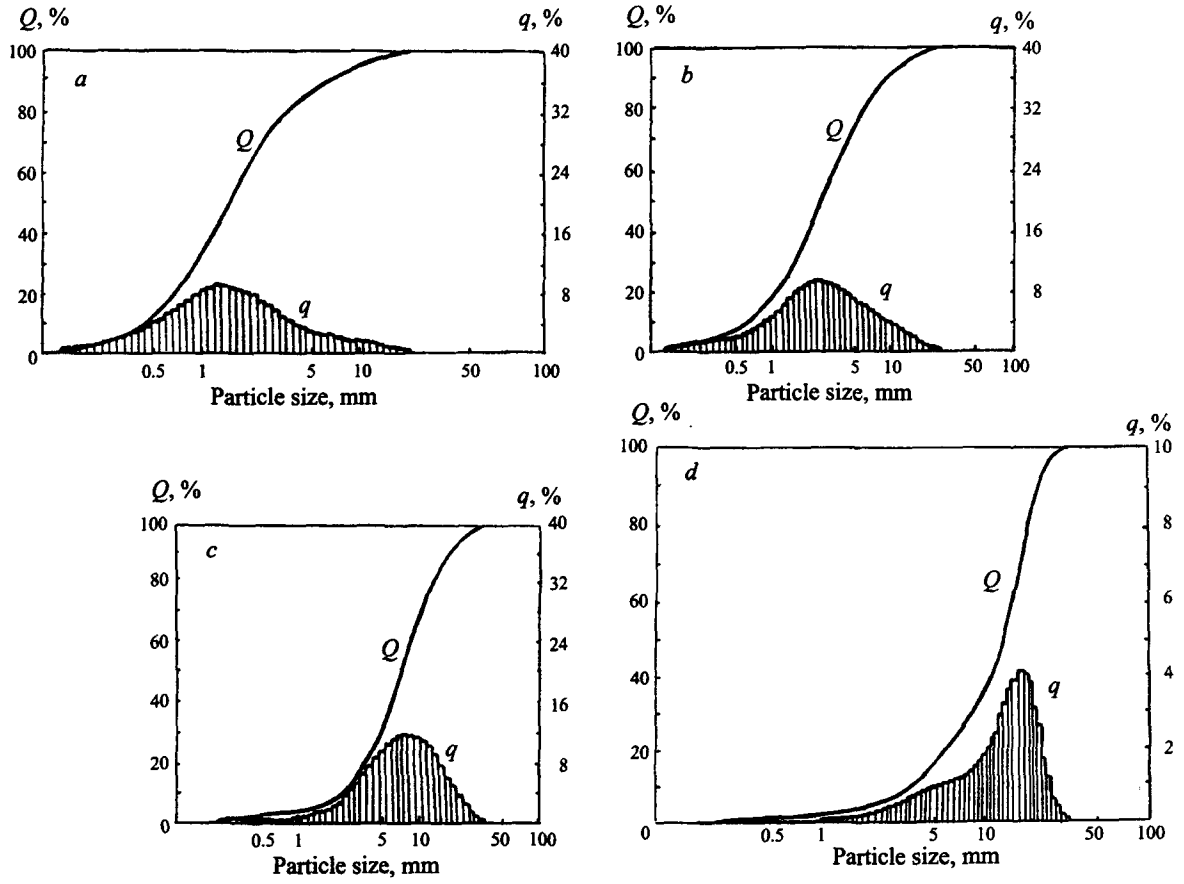

Fig. 3. Integral Q and differential q curve of the size distribution of $LaCrO_3$ powder particles synthesized over the volume at a temperature of 900°C with PVA : $LaCrO_3$ equal to 1 : 1 (*a*), 0.6 : 1 (*b*), 0.3 : 1 (*c*), and at a temperature of 800°C with PVA : $LaCrO_3$ equal to 0.3 : 1 (*d*).

that crystallization does not yet occur in calcination of the gel at a temperature not higher than 500°C. The grains are united in branched chains typical of xerogel (Fig. 4). The size distribution of the grains is abnormal, with the difference reaching 5 – 10 times. The colonies of particles linked in chains retain the structure of the xerogel that is their precursor. Numerous large grains constituting laminar aggregates with a loose surface are found.

With a calcination temperature equal to 800°C, the chain structure of the xerogel disintegrates, and the lanthanum chromite is crystallized. The granular composition of the powder obtained is sufficiently homogeneous. At the same time, the large particles are more isometric than the small particles constituting the fragments of the broken chain structure of the xerogel. A comparison of the powder synthesized and the powder obtained by vibration-crushing of elec-

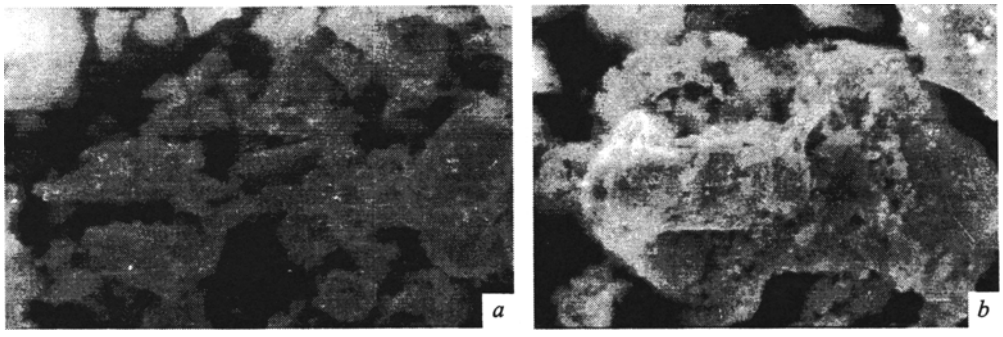

Fig. 4. Microstructure of xerogel with PVA : $LaCrO_3$ equal to 0.3 : 1 heat treated at temperature of 500°C: *a*) chain structure (× 3000); *b*) coarse grain (× 4100).

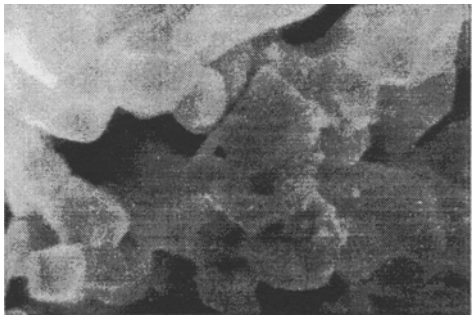

Fig. 5. Microstructure of a sintered ceramic sample made of $LaCrO_3$ synthesized with the sol-gel method (× 6600).

trically melted lanthanum chromite revealed that the powder synthesized in the presence of PVA gel can be an alternative option to the traditionally produced melted lanthanum chromite.

Experimental ceramic articles were prepared from lanthanum chromite powder synthesized by the sol-gel method. The microscopic analysis of the fracture surface of a ceramic sample exhibited good sintering of the grains with preservation of genetic chains of sintered grains of gel origin (Fig. 5).

The lanthanum chromite powder synthesized by the sol-gel method was used to manufacture the outlet part of miniature electric heaters with one-sided current supply intended for service in a URN set for growing single crystals of refractory compounds.

Thus, using aqueous solutions of lanthanum and chrome nitrates in the presence of PVA gel, it is possible to obtain highly disperse lanthanum chromite powder homogeneous in composition and in size. The optimum parameters of the process are as follows: $La(NO_3)_3 \cdot 6H_2O$ and $Cr(NO_3) \cdot 9H_2O$, PVA : $LaCrO_3$ = 0.3 : 1, gel calcination temperature = 900°C.

REFERENCES

1. *Compounds of Rare-Earth Elements. Sulfates, Selenates, Tellurates, Chromates* [in Russian], Nauka, Moscow (1986).
2. S. F. Pal'guyev, V. K. Gilderman, and V. I. Zemtsov, *High-Temperature Electronic Conductors for Electrochemical Equipment* [in Russian], Nauka, Moscow (1990).
3. A. S. Vlasov, L. M. Krainova, "Use of sol-gel processes in ceramic technology," *Tr. D. I. Mendeleev Chem. Eng. Inst.*, Issue 153, 110 – 115 (1988).
4. *Inorganic Chromium Compounds. Reference Book*, Khimiya, Leningrad (1981).
5. *Compounds of Rare-Earth Elements. Carbonates, Oxalates, Nitrates, Titanates* [in Russian], Nauka, Moscow (1984).